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Exploring CH-Activation Pathways in Bifunctional Zirconocene/Borane Systems

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Abstract: The dimethylsilanediyl-bridged ansa-zirconocene dichloride **1**, that contains a pendent allyl substituent at a Cp-ring, adds $HB(C_6F_5)_2$ to the vinyl group to yield the bifunctional zirconocene/borane complex **2**. Substituted benzimidazoles were added to the strongly electrophilic borane moiety as protective groups, which allowed subsequent chloride versus $-CH_2SiMe_3$ exchange at zirconium to take place by treatment with the respective alkyllithium reagent. Alternatively, the introduction of active σ-ligands at zirconium is carried out first, followed by the hydroboration reaction. This route was followed for the synthesis of the diphenyl-ansa-zirconocene/borane complex **12**. Complex **12** reacts slowly in solution by intramolecular electrophilic attack of the borane at its adjacent Cp-ring, followed by deprotonation using a [Zr]−Ph group to yield the zwitterionic complex **14** featuring a borata-tetrahydroindenyl moiety as part of the ansa-metallocene framework. Complex **14** was characterized by X-ray diffraction. It adds PMe_3 at zirconium to yield **15**. Thermolysis of **12** with excess PMe_3 leads to the formation of the (aryne)zirconocene complex **18**, which is stabilized by PMe_3 coordination to zirconium and PMe_3 addition to boron. *N*-Methylbenzimidazole adds to the $-B(C_6F_5)_2$ unit of **12** to give the 1:1 adduct **19**. Thermolysis of **19** at 80 °C in benzene solution in the presence of one additional equivalent of *N*-methylbenzimidazole results in deprotonation of the substrate to yield the σ-*N*-methylbenzimidazolyl zirconium complex **20** (as a mixture of two diastereoisomers). An additional *N*-methylbenzimidazole ligand is bonded to the $B(C_6F_5)_2$ unit in this product.

Introduction

Enzymatic functionalization (or oxidation) of carbon–hydrogen bonds often follows pathways different from those established and used in organic synthesis.[1] In nature's catalysts, substrate orientation and substrate/active site proximity are often more important than an intrinsic intramolecular activation of CH bonds by adjacent functional groups in the substrate. Thus, selective transformations at seemingly "unactivated" positions are often achieved in enzymatic processes with apparent ease. The search for artificial catalysts that exhibit a similar behavior has led to the discovery of a variety of metal catalyst systems that can selectively attack C−H bonds (and sometimes C−C bonds) in hydrocarbon substrates.[2] Their selectivity features, however, often rely on thermodynamic preference or selectivity being effected by specific kinetic control.[3–6] Proximity control

Scheme 1
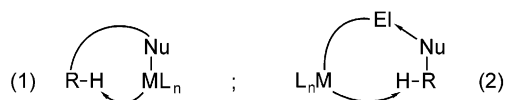
has, of course, often been observed in selective metal-mediated attack on C−H bonds,[7] but most such systems involve hydrocarbon core systems with pendent nucleophilic (e.g., alkylphosphino) groups to which the active metal systems were attached.[8,9] Much of the knowledge assembled about spatial effects in metal-induced C−H (and C−C) activation was derived from studying such systems, but their actual C−H activation processes are usually limited to functionalization of the ligand systems themselves (see example 1 in Scheme 1).[10]

† To whom correspondence should be addressed regarding X-ray crystal structure analyses.

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Scheme 2
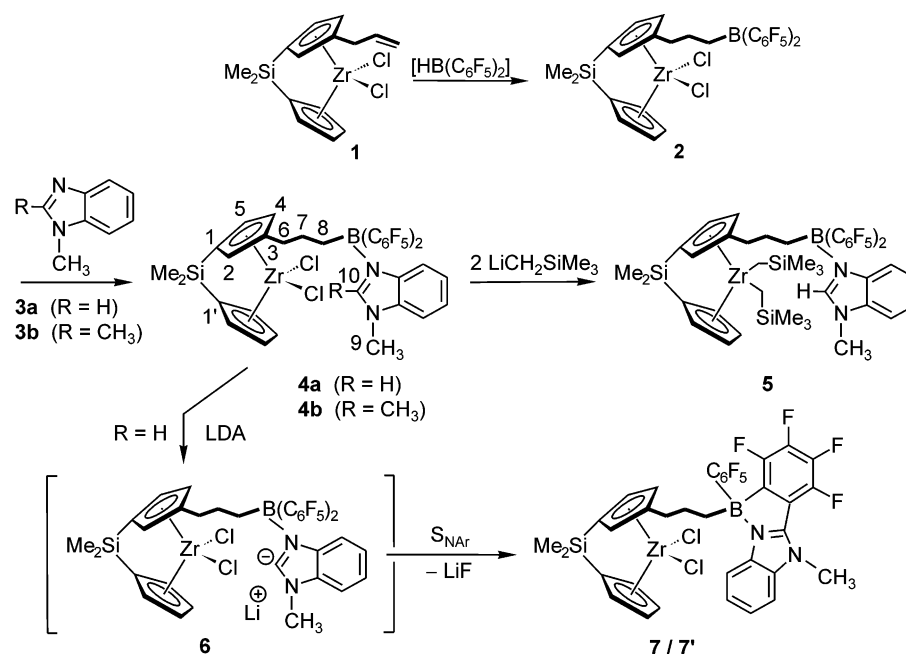
As an attractive alternative, one might envision the synthesis of a metal complex system that itself contains a pendent functionality that is able to bind an incoming substrate and orient it in the proximity of the active metal site as required for a selective activation process. Using an electrophilic "anchoring" group would be attractive because this would allow for (reversible) binding of a great variety of organic substrates through a number of nucleophilic donor functionalities. We have begun to design and synthesize such systems (see example 2 in Scheme 1) that are complementary to many such approaches described in the literature. We have not arrived at a catalytic system so far, but made a number of interesting observations on this route that will be described below.

Results and Discussion

Initial Experiments. Our synthetic aproach was based on an ansa-zirconocene system that contained a pendent very electrophilic $-B(C_6F_5)_2$ borane group that was connected by a trimethylene linker to one of its cyclopentadienide ligands. As we had previously described,[11] the respective zirconocene dichloride complex (**2**) was prepared by treatment of the Cp-allyl-containing ansa-zirconocene dichloride precursor (**1**)[12] with "Piers' borane" $[HB(C_6F_5)_2]$.[13] This resulted in a clean hydroboration reaction to yield the bifunctional complex **2** (see Scheme 2).[14,15]

The problem that we faced next was to achieve a selective functionalization at the transition metal center without affecting the electrophilicity of the pendent borane group. Because chloride versus alkyl anion exchange at the stage of the bifunctional electrophilic system **2** was to be effected by treatment with, for example, an alkyllithium or a Grignard reagent, we needed to develop a protective group scheme, which is, of course, a common feature in organic synthesis, but almost completely unexplored in organometallic chemistry.

For this purpose, we reacted the bifunctional complex **2** with *N*-methylbenzimidazole (**3a**). Treatment of **2** with the hetero-cycle **3a** in toluene at ambient temperature gave the adduct **4a** in almost quantitative yield.[16] The ^{11}B NMR spectrum of the product indicated that the benzimidazole nucleophile had cleanly added to the boron atom. Complex **4a** features a broad ^{11}B NMR resonance at $\delta -5.56$ ($\nu_{1/2} = 324$ Hz) that is very typical of tetravalent boron adduct formation[17] [cf. **2**: ^{11}B NMR: $\delta +75.6$ ($\nu_{1/2} = 1085$ Hz)]. Also, the pair of C_6F_5 substituents at boron in **4a** has become diastereotopic [^{19}F NMR signals at: $\delta -132.2/133.1$ (*o*), $\delta -164.0/-164.1$ (*m*), $\delta -158.8/-159.1$ (*p*)] due to the element of planar chirality of the adjacent metallocene [in contrast to the single set of C_6F_5 resonances at the planar-tricoordinate boron atom of **2**: $\delta -130.2$ (*o*), -160.8 (*m*), -148.6 (*p*)], and the typical upfield shift of the *p*-C_6F_5 ^{19}F NMR was observed upon borane adduct formation[16] to yield **4a**.

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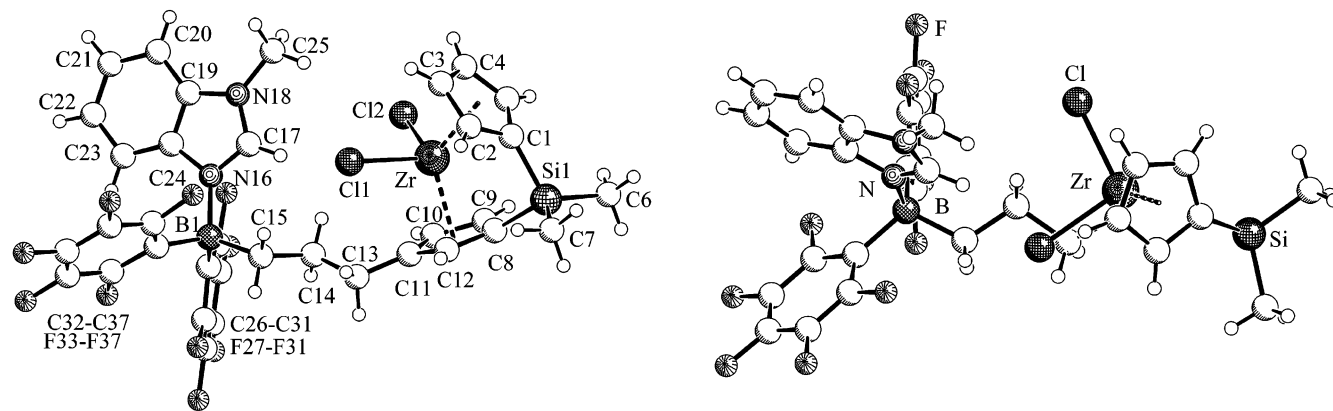
Figure 1. Two views of the molecular structure of complex **4a** in the crystal. Selected bond lengths (Å) and angles (deg): Zr−Cl1 2.438(1), Zr−Cl2 2.426(1), Si1−C1 1.876(3), Si−C6 1.842(3), Si−C7 1.850(3), Si−C8 1.873(3), C11−C13 1.493(4), C13−C14 1.547(4), C14−C15 1.528(4), C15−B1 1.624(4), B1−N16 1.607(4), B1−C26 1.653(4), B1−C32 1.658(4), N16−C17 1.319(3), N16−C24 1.409(3), C17−N18 1.337(3), N18−C19 1.382(3), N18−C25 1.462(4), C19−C24 1.391(4); Cl1−Zr−Cl2 98.93(3), C1−Si1−C8 93.7(1), C1−Si1−C6 112.6(2), C1−Si1−C7 110.7(2), C8−Si1−C6 112.8(1), C8−Si1−C7 112.0(2), C6−Si1−C7 113.5(2), C11−C13−C14 117.1(2), C13−C14−C15 111.4(2), C14−C15−B1 118.9(2), C15−B1−N16 110.0(2), C15−B1−C26 108.4(2), C15−B1−C32 111.4(2), N16−B1−C26 109.7(2), N16−B1−C32 103.0(2), C26−B1−C32 114.2(2), B1−N16−C17 126.3(2), B1−N16−C24 127.6(2), C24−N16−C17 106.0(2), N16−C17−N18 112.5(2), C17−N18−C19 107.4(2).

Similarly, treatment of **2** with 1,2-dimethylbenzimidazole (**3b**) gave the corresponding 1:1 adduct **4b** (97% isolated, for details see the Experimental Section).

Complex **4a** was characterized by X-ray diffraction. It features a typical ansa-metallocene core. To one of its Cp-rings is the −(CH$_2$)$_3$−B(C$_6$F$_5$)$_2$ moiety attached. The *N*-methylbenzimidazole unit[18] has added to the electrophilic boron center by means of its "imine-type" nitrogen center. The resulting boron− nitrogen linkage is strong. The B−N16 bond length (1.607(4) Å) is shorter than the adjacent B−C linkages (e.g., B−C15: 1.624(4) Å). The topology of the system positions the −(CH$_2$)$_3$-[B] unit at the front of the bent metallocene wedge. Nevertheless, it is remarkable that the observed conformational arrangement of the −(CH$_2$)$_3$−B(*N*-methylbenzimidazole)(C$_6$F$_5$)$_2$ unit in the crystal is such that it brings the functionalized end of the benzimidazole ligand into a direct spatial opposition with the open ZrCl$_2$ side of the group 4 bent metallocene (see Figure 1).[14] This is achieved by an appropriate rotation of the C−C bonds of the trimethylene linker (dihedral angles C10−C11− C13−C14: −34.3(4)° and C11−C13−C14−C15: −147.5(2)°).

The C13−C14−C15−B orientation is close to antiperiplanar ($\theta = -176.7(2)°$), but the torsion angles C14−C15−B−N16 and C15−B1−N16−C17 amount to −71.3(3)° and 3.8(4)°, respectively. The Zr•••B distance in complex **4a** is 6.228 Å. In this conformational arrangement, the imidazole N−C(H)═N methine unit (C17−H in Figure 1) is even closer to zirconium (Zr•••C17: 4.877 Å) and the adjacent Zr-bound chloride ligands (Zr−Cl1: 2.438(1) Å, Zr−Cl2: 2.426(1) Å), featuring distances of 3.492 Å [(Zr)Cl1••C17] and 4.173 Å [(Zr)Cl2••C17], respectively.

The reaction of the adduct **4a** with 2 mol equiv of LiCH$_2$- SiMe$_3$ in ether (−20 °C to room temperature) proceeded cleanly with metathetical exchange of both chloride ligands at zirconium. The benzimidazole-protected −B(C$_6$F$_5$)$_2$ Lewis acid was left untouched under these conditions. The product **5** (94% isolated) showed typical AB quartetts of the two −CH$_2$SiMe$_3$ pairs of hydrogens in the ¹H NMR spectrum (δ 0.05/−0.10, δ −0.04/−0.29; corresponding ¹³C NMR signals at δ 35.0 and δ 38.4). The ¹¹B NMR resonance was found at δ −5.16. Complex **5** proved rather stable. Even heating to ca. 90 °C did not result in an intramolecular attack of the bulky σ-ligands at the adjacent benzimidazole system.

We tried to mimick such a reaction by treatment of **4a** with LDA. When the reaction was carried out in tetrahydrofuran, we observed the formation of the product **7** (see Scheme 2). This indicated that the coordinated benzimidazole system was deprotonated under these conditions, and the resulting carbanion (**6**) did not react intramolecularly with the [Zr]Cl$_2$ unit but rather underwent a nucleophilic aromatic substitution reaction at one of the adjacent C$_6$F$_5$ ring systems. A similar reaction had previously been observed with a benzimidazole/B(C$_6$F$_5$)$_3$ adduct to occur under similar reaction conditions.[19,20]

In this reaction, a chirality center at boron is introduced in addition to the persistent planar chirality element of the bent

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metallocene. Therefore, two diastereoisomers **7/7′** were formed in a ca. 1:1 ratio. These gave rise to the observation of doubled sets of a number of signals in the NMR spectra [e.g., N−CH$_3$: δ 4.34/4.32, both showing a long-range J_{HF} coupling of 3.4 Hz that is typical for this general framework[19,21]); C$_6$F$_5$ (^{19}F NMR): δ −133.5/−134.2 (*o*), δ −160.2/−161.1 (*p*), δ −165.5/−165.9 (*m*)], while others were isochronous for the two diastereomers [e.g., C$_6$F$_4$ (^{19}F NMR): δ −132.6, −135.8, −151.7, −159.3; ^{11}B NMR: δ −4.0].

Preparation and Reactions of Bifunctional Diphenylzirconocene/Borane Complexes. Diphenylzirconocenes allow for several pathways of activation.[22] Among them, thermally induced (aryne)zirconocene formation[23−25] gives reactive intermediates that had previously been used in CH-activation reactions.[22,26] For the synthesis of a bifunctional diphenylzirconocene/borane system, we first reacted the alkyl-Cp-containing ansa-metallocene complex **1** with phenyllithium to yield **8**. At 80 °C, complex **8** loses 1 equiv of benzene. The NMR spectra of the resulting solution indicate that the (aryne)zirconocene (**9**) had probably been formed as a reactive intermediate that was rapidly trapped by the internal Cp-bonded olefin[27] to form **10**. Complex **10** was generated on a preparative scale in the presence of excess PMe$_3$[24] to avoid side reactions and then directly quenched[28] by treatment with the anilinium Brønsted acid [PhNMe$_2$H]$^+$Cl$^-$ to yield **11**, as expected as a single diastereoisomer (Scheme 3).

Complex **8** was then reacted with HB(C$_6$F$_5$)$_2$. In principle, this strongly Lewis acidic borane might have been able to abstract a phenyl anion equivalent from zirconium.[29] However, this is not observed, but a clean hydroboration of the pendent C=C double bond takes place to give **12** (Scheme 4). Complex **12** shows a ^{11}B NMR resonance at δ +79.2, which is characteristic for a free tricoordinate borane, and three typical ^{19}F NMR signals corresponding to the pair of symmetry equivalent C$_6$F$_5$ substituents at boron [δ −129.7 (*o*), −147.5 (*p*), −160.9 (*m*)]. The ^{1}H/^{13}C NMR spectra show the presence of two nonequivalent phenyl substituents at the zirconium center.

Complex **12** is not stable for prolonged time at ambient temperature in solution. During ca. 3 d, it loses 1 equiv of
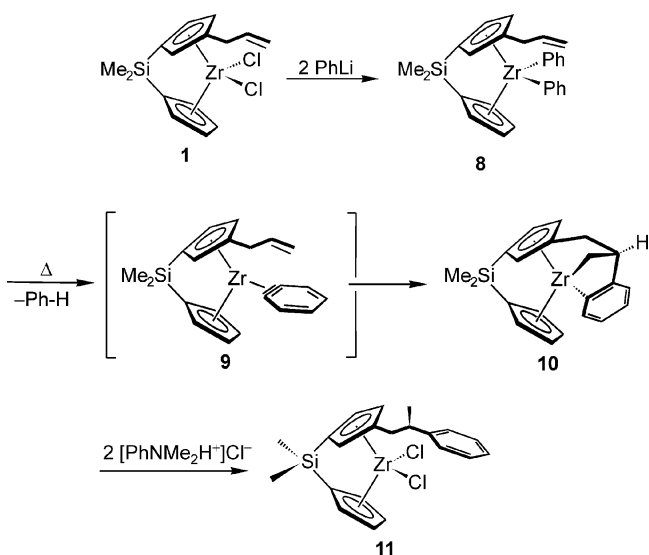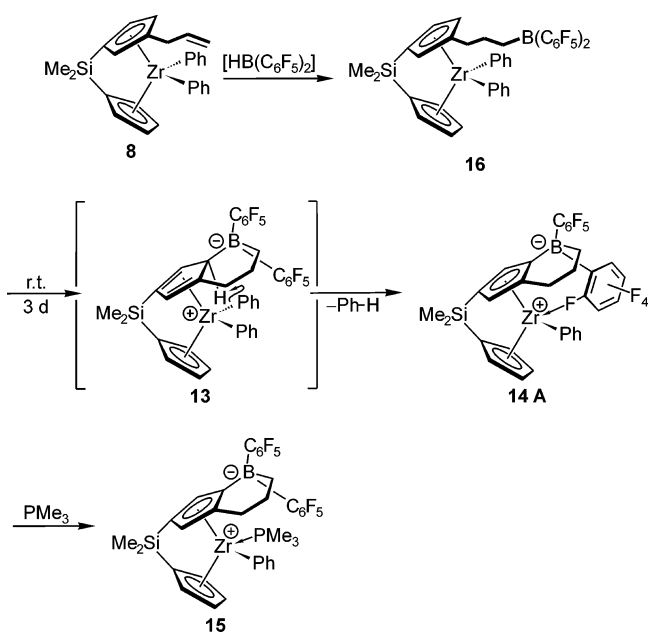
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Scheme 3

Scheme 4

benzene with the formation of **14**.[30] The dipolar product **14** contains a strongly electrophilic zirconium center, to which PMe$_3$ could be added. We isolated the addition product **15** as a single isomer in 89% overall yield, starting from **8**.

Complex **12** contains a pair of σ-ligands at zirconium and a strongly electrophilic −B(C$_6$F$_5$)$_2$ Lewis acid in close vicinity. It is remarkable that even in this situation σ-ligand transfer from zirconium to boron does not take place. Instead, complex **12** utilizes the strongly electrophilic pendent −B(C$_6$F$_5$)$_2$ moiety to enter into a different reaction pathway. It is apparently initiated by −B(C$_6$F$_5$)$_2$ addition to the adjacent Cp-ring from the "outside" to generate the intermediate **13**. This has the *ipso*-hydrogen atom pointing toward the "inside" of the former metallocene system, which brings an acidified hydrogen into close proximity of zirconium bound σ-phenyl ligand. Its kinetic basicity is apparently sufficient to abstract the proton with

(30) Preliminary communication: Hill, M.; Kehr, G.; Erker, G.; Kataeva, O.; Fröhlich, R. *Chem. Commun.* **2004**, 1020−1021.
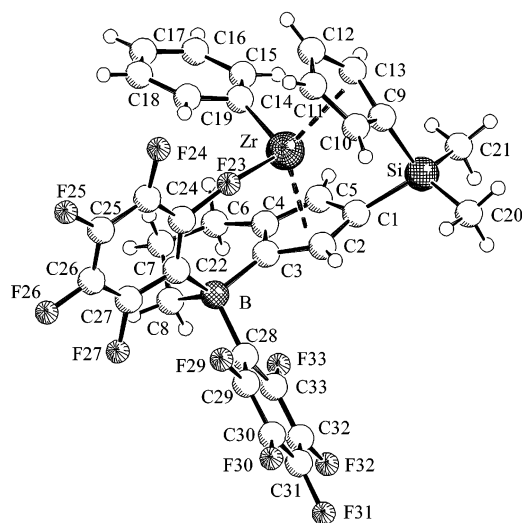
Figure 2. A view of the molecular structure of complex **14**. Selected bond lengths (Å) and angles (deg): Zr–F23 2.250(1), Zr–C14 2.203(2), Si1–C1 1.871(2), Si–C20 1.849(2), Si–C21 1.855(2), Si–C9 1.872(2), C3–B 1.627(3), C8–B 1.649(3), B–C22 1.663(3), B–C28 1.665(3), C23–F23 1.410(2); F23–Zr–C14 113.03(7), C1–Si–C9 93.8(1), C1–Si–C20 113.5-(1), C1–Si–C21 110.9(1), C9–Si–C20 110.8(1), C9–Si–C21 112.8(1), C20–Si–C21 113.5(1), C2–C3–B 130.5(2), C7–C8–B 111.4(2), C3–B–C8 106.7(2), C3–B–C22 115.3(2), C3–B–C28 106.2(2), C8–B–C22 105.6(2), C8–B–C28 111.6(2), C22–B–C28 111.5(2), Zr–F23–C23 142.8(1).

formation of benzene and the observed product **14**.[31] Complex **12** represents a rare example where electrophilic borane addition to the adjacent cyclopentadienyl ring is favored over σ-ligand abstraction.

Complex **14** was characterized by X-ray diffraction (see Figure 2). It shows that the –B(C_6F_5)$_2$ electrophile has attacked the adjacent Cp-ring to close a six-membered heterocycle (C3–B: 1.627(3) Å). This has created a dipolar structural framework. One of the phenyl groups has remained at zirconium (Zr–C14: 2.203(2) Å). The anellated six-membered ring of the borate tetrahydroindenyl moiety of complex **14** attains a slightly distorted half-chair conformation. As is illustrated by the projection of **14** as depicted in Figure 3, this has led to a differentiation of the C_6F_5 substituents at boron. The equatorial C_6F_5 ring [dihedral angle C2–C3–B–C28: –41.8(3)°] becomes oriented away from the core of the complex, whereas this specific conformational arrangement brings the axial C_6F_5 ring (θ C2–C3–B–C22: 82.2(2)°) close toward the inside of the metallocene. This has allowed one of the (aryl)C–F ortho fluorine atoms to bind to the electrophilic zirconium center. The resulting (aryl)C–F–Zr linkage is rather strong (Zr–F23 2.250-(1) Å, C23–F23–Zr: 142.8(1)°).[32,33] Consequently, the C23–F23 bond (1.410(2) Å) is markedly elongated as compared to the average bond length of the remaining ortho-(aryl)-C–F bonds in **14** (1.353(2) Å).
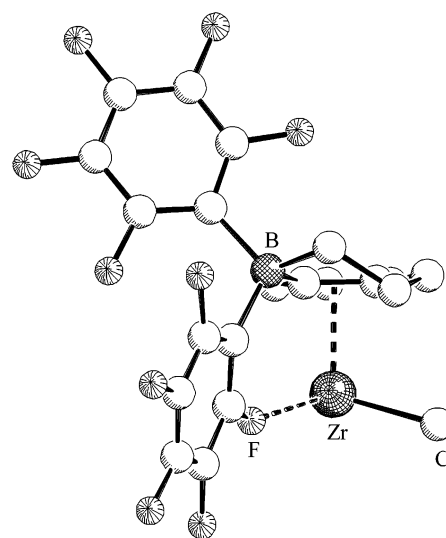
Figure 3. A projection of the molecular geometry of complex **14** showing the half-chair-like conformational arrangement of the tetrahydroboratain-denyl part of the ligand system (parts of the molecule were omitted for clarity).

Complex **14** features dynamic NMR spectra, which arise from a conformational equilibration of the boratatetrahydroindenyl part of the system. This is best illustrated by the temperature-dependent ^{19}F NMR spectra of **14**. At ambient temperature, three pairs of signals are observed, corresponding to the ortho (δ –116.6/–130.0)-, para (δ –156.0/–153.2)-, and meta (δ –161.3/–162.7)-F-substituents of the cis- and trans-C_6F_5 groups of the rapidly equilibrating system. Lowering the temperature leads to decoalescence and the appearance of two separate sets of ^{19}F NMR signals that originate from two nonidentical conformers. The major conformer (**14A**) exhibits a total of 10 separate ^{19}F NMR resonances (see Figure 4). This indicates that under these conditions (233 K, 564 MHz) the rotation of both C_6F_5 rings around the B–C(sp^2) bonds is frozen on the NMR time scale. Most remarkable is the observation of one ortho-C_6F_5 signal at a very negative δ-value of –175.4[33] [remaining signals of this C_6F_5 ring at δ –126.2 (o), δ –156.8 (p), δ –155.6 and δ –164.2 (m); resonances of the second C_6F_5 substituent at δ –131.2, –132.1 (o), δ –160.0 (p), δ –162.8, –164.6 (m)]. We assume that the conformer **14A** corresponds to the structure observed in the solid state (see above). From the coalescence of the ^{19}F NMR resonances of the pair of o-F substituents [$T_c ≈ 283$ K, Δν (213 K) = 27 800 Hz], we estimated an activation energy of this exchange process of $ΔG^‡$-(T_c) ≈ 10.5 ± 1.0 kcal/mol. This value must be regarded to be close to the Zr···F(C) bond dissociation energy of **14A**. The other conformational (**14B**) isomer shows five ^{19}F NMR signals of a static C_6F_5 substituent [δ –108.6/–111.2 (o), δ –154.7

(31) See for a comparison: Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem.* **1996**, *108*, 108–110; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80–82. Sun, Y.; Piers, W. E.; Rettig, S. J. *Organometallics* **1996**, *15*, 4110–4112. Pindado, G. J.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1997**, 609–610. Pindado, G. J.; Thornton-Pett, M.; Bouwkamp, M.; Meetsma, A.; Hessen, B.; Bochmann, M. *Angew. Chem.* **1997**, *109*, 2457–2460; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2358–2361. Pindado, G. J.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 3115–3127. Pindado, G. J.; Thornton-Pett, M.; Hursthouse, M. B.; Coles, S. J.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1999**, 1663–1668. Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U.; Burlakov, V. V.; Shur, V. B. *Angew. Chem.* **2003**, *114*, 1455–1458; *Angew. Chem., Int. Ed.* **2003**, *42*, 1414–1418.

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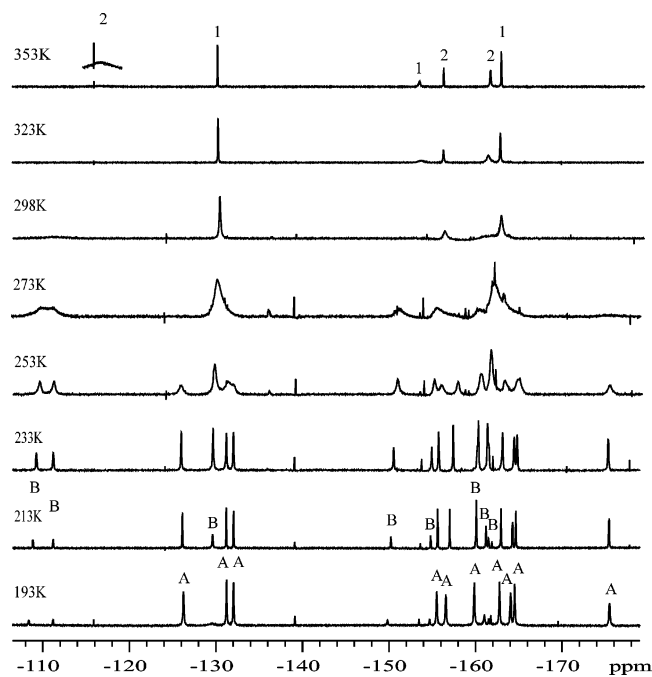
Figure 4. Dynamic ^{19}F NMR spectra (564 MHz) of complex **14**. The numbers 1 and 2 denote the resonances of the *cis*- and *trans*-C_6F_5 ring systems at high temperature. The letters A and B mark C_6F_5 resonances of the two conformational isomers **14A** and **14B** at low temperature.

Scheme 5. Equilibration of the Dipolar Metallocene Conformers **14b** $\leftrightharpoons$ **14B** (Only the Inversion of the Boratatetrahydroindenyl Part of the Molecule Is Depicted)

14 A (major)   **14 B (minor)**
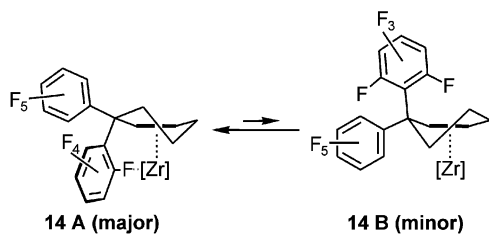
(p), δ $-160.0/-161.5$ (m)] and three ^{19}F NMR resonances [δ -129.6 (o), δ -150.0 (p), δ -161.1 (m)] of a freely rotating C_6F_5 group at 203 K. The **14A** $\leftrightharpoons$ **14B** equilibrium is slightly temperature dependent. The amount of the minor isomer **14B** decreases with decreasing temperature. We assume that we have here observed the ring inversion process of the boratatetrahydroindenyl unit (see Scheme 5). The **14A** to **14B** rearrangement brings both C_6F_5 substituents in positions that do not enable them to build up a slightly stabilizing (aryl)C$-$F$-$metal interaction.

The intramolecular electrophilic aromatic substitution reaction at the Cp-ring of **12** to give **14** is sufficiently slow to allow for a successful competition of a variety of other reactions starting from the bifunctional complex **12**. Thus, it rapidly reacts with *n*-butylisonitrile in toluene at room temperature.[34] Two molar equivalents of the RN$\equiv$C reagent are consumed to yield **16** (Scheme 6). One butylisonitrile is added to the borane (^{11}B

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Scheme 6
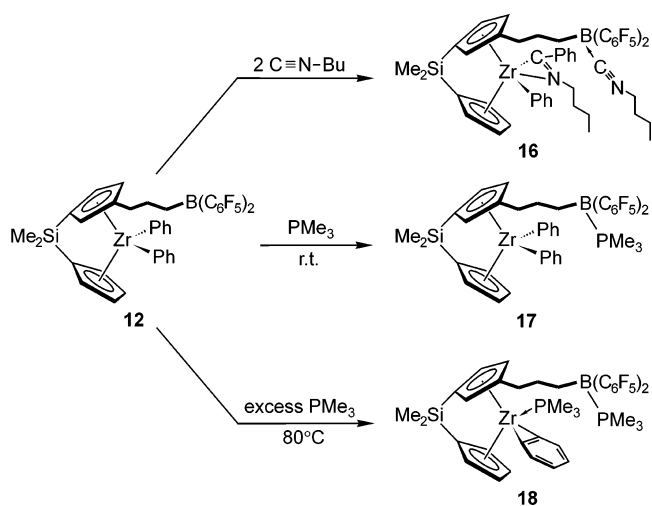
NMR: δ -18.5), and the other is inserted into a Zr$-$Ph moiety to give a single isomer of a (η^2-iminoacyl)zirconium complex.[34,35] The product **16** shows a typical ^{13}C NMR resonance of the iminoacyl carbon atom at δ 240.1. The single remaining σ-phenyl group at the zirconium metal shows very typical ^{13}C NMR features at δ 179.1 (*ipso*), 141.8 (*o*), 126.7 (*m*), and 123.9 (*p*).

Treatment of **12** with PMe$_3$ at room temperature in toluene gave the 1:1 adduct (**17**, 97% isolated). The phosphine was added to the $-$B(C$_6$F$_5$)$_2$ moiety [^{11}B NMR: δ -14.1 ($\nu_{1/2}$ = 258 Hz), ^{31}P NMR: δ -10.2 ($\nu_{1/2}$ = 115 Hz)]. Attachment of the additional PMe$_3$ ligand at boron made the pair of C$_6$F$_5$ groups diastereotopic. This became just experimentally observable by the splitting of the *ortho*-C$_6$F$_5$ resonances [δ $-130.7/-$130.8], while the pair of *para* (δ -158.3)- and *meta*-C$_6$F$_5$ signals (δ -163.6) was not resolved. Complex **17** features the ^1H NMR signals of two σ-phenyl ligands at zirconium [δ 7.52, 7.23, 7.13 (*o*, *m*, *p*) and δ 7.31, 7.20, 7.08].

When complex **12** was kept for 3 h at 80 °C in benzene in the presence of a ca. 10-fold excess of PMe$_3$, the formation of the PMe$_3$-stabilized (aryne)zirconocene complex **18** was observed.[24] A single isomer was obtained (92% isolated). Again, 1 equiv of PMe$_3$ was also added to the B(C$_6$F$_5$)$_2$ group [^{11}B NMR: δ -14.0; ^{19}F NMR: δ $-129.9/-130.3$ (o), $-158.4/-$157.9 (p), $-163.2/-163.1$ (p)]. Consequently, complex **17** features two PMe$_3$ ^{31}P NMR resonances [δ -7.9 ($\nu_{1/2}$ = 7 Hz, [Zr]$-$PMe$_3$) and δ -10.0 ($\nu_{1/2}$ = 120 Hz, [B]$-$PMe$_3$)]. The benzyne ligand shows typical ^{13}C NMR signals of the coordinated carbon centers at δ 178.5 and 157.8.

In-situ-generated **12** also reacts cleanly with *N*-methylbenzimidazole or 1,2-dimethylbenzimidazole. Selective addition to the $-$B(C$_6$F$_5$)$_2$ functional group is observed to give the corresponding 1:1 addition products **19a** and **19b**, respectively, in almost quantitative yield (see Scheme 7). The presence of a pair of inequivalent σ-phenyl ligands at zirconium is revealed by their very characteristic ^{13}C NMR resonances [**19a**: δ 186.1 (*ipso*), 134.4 (*o*), 126.5 (*m*), 125.7 (*p*) and δ 181.7, 136.3, 126.5, 126.1]. The formation of a tetravalent boron compound is apparent from the typical ^{11}B NMR feature (δ -4.5) of **19a**

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Scheme 7

and the observation of the ^{19}F NMR signals of a pair of diastereotopic C_6F_5 groups at the boron atom. The ^{13}C NMR resonance of the NCHN imidazole carbon center (C10 in Scheme 7) occurs at δ 141.2. Complex **19b** features similar NMR spectra [^{13}C NMR: δ 151.8 (C10), ^{11}B: δ −3.3.].

Heating complex **19a** to 80 °C initially resulted in the formation of a pair of new compounds (with formation of benzene). However, the reaction was not clean enough under these conditions, especially with increasing conversion, to allow us to isolate and identify the newly formed products. We tried to potentially stabilize the products by carrying out the reaction in the presence of trimethylphosphine, but this resulted only in the rapid replacement of the weaker benzimidazole donor by the phosphine. Eventually, only the PMe$_3$-stabilized complex **18** was formed in these experiments.

The reaction system became sufficiently clean when we thermolyzed complex **19a** at 80 °C in benzene in the presence of 1 mol equiv of *N*-methylbenzimidazole. After 3 h, the reaction was complete, and we isolated a 3:2 mixture of the diastereo-isomeric products **20A** and **20B** in a combined yield of ca. 90%.

The complexes **20** were formed from **19a** by liberation of 1 equiv of benzene, and the five-membered ring of a *N*-methylbenzimidazole was deprotonated and has become attached to the zirconium center. The remaining σ-phenyl ligand is readily identified by its typical ^{13}C NMR resonances (**20A**: δ 181.4 (*ipso*), 142.0 (*o*), 127.0 (*m*), 124.1 (*p*)]. The newly formed σ-*N*-methylbenzimidazole ligand shows a very characteristic ^{13}C NMR feature of the Zr−C(N$_2$) carbon atom (C10′ in Scheme 7) at δ 202.9.[36,37] In addition, there is one intact *N*-methyl-benzimidazole coordinated to the boron center of complex **20A** [^{11}B NMR: δ −5.1; benzimidazole C10: δ 141.2 (^{13}C), 10-H: δ 7.32 (^{1}H)]. The ^{19}F NMR spectra show the presence of two diastereotopic C_6F_5 groups present in **20A**.

Complex **20B** shows very similar spectra [σ-phenyl: δ 177.2 (^{13}C, *ipso*); Zr−benzimidazolide: δ 202.7 (^{13}C, C10′); B−benz-imidazole: δ 141.2 (^{13}C, C10), δ 7.19 (^{1}H, 10-H)]. Complexes

20A and **20B** are apparently diastereoisomers that differ by their relative configuration of the metal chirality center and the element of planar chirality of the substituted ansa-metallocene backbone.[38]

Conclusions

Our study has shown that bifunctional zirconocene complexes with a pendent strongly Lewis acidic −B(C$_6$F$_5$)$_2$ functional group that contain active σ-ligands at zirconium can be obtained by either of two ways. Some active ligands (e.g., σ-phenyl) can actually be introduced at an early stage of the synthesis, because they have been shown to be resistant to abstraction by both the HB(C$_6$F$_5$)$_2$ reagent and the attached −B(C$_6$F$_5$)$_2$ Lewis acid. Alternatively, the borane is introduced first at the stage of the respective zirconocene dichloride precursor, but then a protective group must be introduced at the boron Lewis acid before σ-ligand exchange at the transition metal center can be carried out. We have described such an example and have shown independently that the protective donor ligand can be removed or exchanged subsequently at the boron center.

The *N*-methylbenzimidazole model substrate is CH-activated by the bifunctional Zr/B system. Unfortunately, direct mecha-nistic evidence is hard to achieve from such a rapidly ligand exchanging system, but it is well conceivable that the in-situ-generated reactive (aryne)zirconocene intermediate has attacked the CH bond of the adjacent benzimidazole whose kinetic acidity has probably been increased considerably by coordination through its "imino" nitrogen atom to boron.[39,40] So it seems that bifunctional transition metal/boron-Lewis acid systems that show some potential for increased CH (or maybe even CC) activation can be easily available by the principal synthetic routes as outlined in this paper. We will try to adapt these successful synthetic entries for the preparation of related systems using other metal/electrophile combinations and additional

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(37) Herrmann, W. A.; Öfele, K.; Elison, M.; Kühn, F. E.; Roesky, P. W. *J. Organomet. Chem.* **1994**, *480*, C7−C9. Kuhn, N.; Kratz, T.; Bläser, D.; Boese, R. *Inorg. Chim. Acta* **1995**, *238*, 179−181. Niehues, M.; Kehr, G.; Erker, G.; Wibbeling, B.; Fröhlich, R.; Blaque, O.; Berke, H. *J. Organomet. Chem.* **2002**, *663*, 192−203. Vagedes, D.; Erker, G.; Kehr, G.; Fröhlich, R.; Grimme, S.; Mück-Lichtenfeld, C. *Z. Naturforsch.* **2003**, *58b*, 305−310.

(38) For a comparison, in an NMR experiment, the unfunctionalized parent system [Me$_2$Si(C$_5$H$_4$)$_2$]ZrPh$_2$ was treated with a 6-fold excess of *N*-methylbenzimidazole in d_6-benzene at 80 °C to yield the corresponding reaction product [Me$_2$Si(C$_5$H$_4$)$_2$]Zr(Ph)(*N*-methyl-2-benzimidazolyl) [^{13}C NMR δ 202.5 (C10′)] plus benzene. Under these conditions, this reaction took ca. 7 h to go to completion, which makes it ca. 5−7 times slower than the corresponding **19a** to **20** transformation.

(39) Röttger, D.; Erker, G.; Fröhlich, R.; Kotila, S. *J. Organomet. Chem.* **1996**, *518*, 17−19.

(40) Ren, J.; Workman, D. B.; Squires, R. R. *Angew. Chem.* **1997**, *109*, 2330−2332; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2230−2232.

activation/protection protocols to hopefully arrive eventually at some synthetically useful CH (or CC)-activating systems that utilize such specific proximity effects.

Experimental Section

All reactions with organometallic compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. The following instruments were used for physical characterization of the compounds: Melting points, DSC 2010 TA-Instruments; elemental analyses, Foss-Heraeus CHNO-Rapid and Vario El III Mikro elemental analyzer; IR, Nicolet 5 DXC FT IR spectrometer; NMR, Bruker AC 200 P (^{1}H: 200.13 MHz, ^{13}C: 50.32 MHz, ^{11}B: 64.21 MHz) or Varian UNITY plus NMR spectrometer (^{1}H: 599.8 MHz, ^{13}C: 150.8 MHz, ^{19}F: 564.3 MHz).

X-ray crystal structure analyses: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius, B. V., 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33−37. Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics SCHAKAL (Keller, E. Universität Freiburg, 1997).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 232735 (**4a**) and 229733 (**14a**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

Complexes **1**[11] and **2**[14] were prepared as we have previously described in the literature. HB(C$_6$F$_5$)$_2$ was synthesized as described by Piers et al.[13] For atom numbering, see Scheme 2.

Reaction of Complex 2 with *N*-Methylbenzimidazole; Preparation of Adduct 4a. Complex **2** (1.10 g, 1.50 mmol) and 1-methylbenzimidazole (0.20 g, 1.50 mmol) were dissolved together in 50 mL of toluene at ambient temperature. After 2 h, the solvent was removed in vacuo to give **4a** as a yellow solid (1.24 g, 95%). Single crystals for the X-ray crystal structure analysis of **4a** were obtained from a concentrated toluene solution, mp 194 °C. Anal. Calcd for C$_{35}$H$_{27}$N$_2$-BF$_{10}$Cl$_2$SiZr (866.6): C, 48.51; H, 3.14; N, 3.23. Found: C, 48.92; H, 3.32; N, 3.06. ^{1}H NMR (d_8-toluene, 600 MHz, 300 K): δ 8.27 (s, 1H, 10-H), 7.66 (m, 1H, 13-H), 6.81 (m, 2H, 14-H, 15-H), 6.72 (m, 1H, 3-H′), 6.67 (m, 1H, 4-H′), 6.47 (m, 1H, 16-H), 6.42 (m, 1H, 4-H), 5.40 (m, 1H, 5-H′), 5.33 (m, 1H, 2-H′), 5.30 (m, 1H, 5-H), 5.11 (m, 1H, 2-H), 2.89/2.78 (each m, each 1H, 6-H, 6-H′), 2.76 (s, 3H, 9-H), 1.83/1.76 (each m, each 1H, 8-H, 8-H′), 1.55 (m, 2H, 7-H), 0.13/0.07 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_8-toluene, 150 MHz, 300 K): δ 148.8 ($^1J_{CF}$ = 238.1 Hz, *o*-C of C$_6$F$_5$), 143.1 (C3), 141.8 (C10), 139.5 ($^1J_{CF}$ = 250.9 Hz, *p*-C of C$_6$F$_5$), 137.5 ($^1J_{CF}$ = 249.8 Hz, *m*-C of C$_6$F$_5$), 136.6 (C12), 132.9 (C17), 128.7 (C4′), 128.3 (C4), 125.7 (C3′), 125.3 (C14), 125.2 (C15), 121.8 (broad, *ipso*-C of C$_6$F$_5$), 116.5 (C13), 114.4 (C2′), 114.3 (C2), 114.1 (C5), 112.8 (C5′), 111.0 (C16), 107.9 (C1′), 107.6 (C1), 33.0 (C6), 31.9 (C9), 26.2 (C7), 23.8 (C8), −5.7/−6.5 (Si(CH$_3$)$_2$). ^{11}B{^{1}H} NMR (d_8-toluene, 64 MHz, 298 K): δ −5.56 ($ν_{1/2}$ = 324 Hz). ^{19}F NMR (d_8-toluene, 564 MHz, 300 K): δ −132.2 (m, 2F, *o*-F of C$_6$F$_5$), −133.1 (m, 2F, *o*-F′ of C$_6$F$_5$), −158.8 (t, $^3J_{FF}$ = 20.7 Hz, 1F, *p*-F of C$_6$F$_5$), −159.1 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-F′ of C$_6$F$_5$), −164.0 (m, 2F, *m*-F of C$_6$F$_5$), −164.1 (m, 2F, *m*-F′ of C$_6$F$_5$). X-ray crystal structure analysis of complex **4a**: formula C$_{35}$H$_{27}$BCl$_2$F$_{10}$N$_2$-SiZr, *M* = 866.61, colorless crystal 0.30 × 0.30 × 0.25 mm, *a* = 20.170(1), *b* = 14.898(1), *c* = 23.905(1) Å, *β* = 92.44(1)°, *V* = 7176.8(7) Å^3, $ρ_{calc}$ = 1.604 g cm^{-3}, *μ* = 5.70 cm^{-1}, empirical absorption

correction (0.848 ≤ *T* ≤ 0.871), *Z* = 8, monoclinic, space group *C*2/*c* (No. 15), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 23 838 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.68 Å^{-1}, 8969 independent (R_{int} = 0.042) and 5488 observed reflections [*I* ≥ 2 *σ*(*I*)], 472 refined parameters, *R* = 0.043, w*R*^{2} = 0.092, max. residual electron density 0.32 (−0.45) e Å^{-3}, hydrogens calculated and refined as riding atoms.

Reaction of Complex 2 with 1,2-Dimethylbenzimidazole; Preparation of 4b. A solution of 1,2-dimethylbenzimidazole (0.24 g, 1.64 mmol) in 10 mL of toluene was added to a solution of 1.20 g (1.63 mmol) of **2** in 20 mL of toluene at ambient temperature. After 2 h at room temp, the solvent was removed in vacuo to yield 1.38 g (96%) of complex **4b** as a pale yellow solid, mp 207 °C. Anal. Calcd for C$_{36}$H$_{29}$N$_2$BF$_{10}$Cl$_2$SiZr (880.6): C, 49.10; H, 3.32; N, 3.18. Found: C, 49.25; H, 3.09; N, 3.05. ^{1}H NMR (d_8-toluene, 600 MHz, 300 K): δ 7.43 (m, 1H, 13-H), 6.88 (m, 1H, 15-H), 6.85 (m, 1H, 14-H), 6.65 (m, 1H, 3-H′), 6.62 (m, 1H, 4-H′), 6.60 (m, 2H, 16-H), 6.20 (m, 1H, 4-H), 5.36 (m, 1H, 5-H′), 5.25 (m, 2H, 5-H, 2-H′), 5.01 (m, 1H, 2-H), 2.73 (m, 2H, 6-H), 2.52 (s, 3H, 9-H), 2.09 (s, 3H, 10-Me), 1.95/1.62 (each m, each 1H, 8-H, 8-H′), 1.48/1.12 (each m, each 1H, 7-H, 7-H′), 0.09/0.04 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_8-toluene, 150 MHz, 300 K): δ 152.4 (C10), 148.8 ($^1J_{CF}$ = 241.3 Hz, *o*-C of C$_6$F$_5$), 148.5 ($^1J_{CF}$ = 240.0 Hz, *o*-C of C$_6$F$_5$), 139.9 ($^1J_{CF}$ = 241.5 Hz, *p*-C of C$_6$F$_5$), 139.6 ($^1J_{CF}$ = 242.9 Hz, *p*-C of C$_6$F$_5$), 137.7 ($^1J_{CF}$ = 246.9 Hz, *m*-C of C$_6$F$_5$), 136.6 (C12), 143.6 (C3), 132.6 (C17), 127.9 (C4′), 127.7 (C4), 126.3 (C3′), 124.1 (C14), 124.0 (C15), 116.9 (C13), 114.3 (C5), 114.2 (C2), 114.1 (C2′), 112.6 (C5′), 110.4 (C16), 107.8 (C1′), 107.5 (C1), 33.1 (C6), 29.2 (C9), 26.9 (C7), 23.4 (C8), 12.7 (Me-10), −6.0/−6.9 (Si(CH$_3$)$_2$), *ipso*-C of C$_6$F$_5$ not observed. ^{11}B{^{1}H} NMR (d_8-toluene, 64 MHz, 298 K): δ −3.35 ($ν_{1/2}$ = 491 Hz). ^{19}F NMR (d_8-toluene, 564 MHz, 300 K): δ = −131.6 (m, 2F, *o*-F of C$_6$F$_5$), −131.7 (m, 2F, *o*-F′ of C$_6$F$_5$), −158.3 (t, $^3J_{FF}$ = 20.6 Hz, 1F, *p*-F′ of C$_6$F$_5$), −159.0 (t, $^3J_{FF}$ = 20.8 Hz, 1F, *p*-F of C$_6$F$_5$), −163.5 (m, 2F, *m*-F′ of C$_6$F$_5$), −163.8 (m, 2F, *m*-F of C$_6$F$_5$).

Treatment of Adduct 4a with (Trimethylsilyl)methyl Lithium: Synthesis of Complex 5. A Schlenk flask was charged with complex **4a** (80.6 mg, 93 μmol) and 17.5 mg (186 μmol) of solid Me$_3$SiCH$_2$Li. The mixture was suspended in ether (30 mL) at −20 °C, and then it was allowed to warm to room temperature. After being stirred for 1 h, the solvent was removed in vacuo and the residue was suspended in toluene. It was filtered through Celite, and the clear filtrate was evaporated to dryness to yield 84.8 mg (94%) of complex **5** as a yellow solid, mp 119 °C. Anal. Calcd for C$_{43}$H$_{49}$N$_2$BF$_{10}$Si$_3$Zr (970.1): C, 53.24; H, 5.09; N, 2.89. Found: C, 53.21; H, 4.71; N, 2.55. ^{1}H NMR (d_2-dichloromethane, 600 MHz, 300 K): δ 8.00 (s, 1H, 10-H), 7.62 (d, $^3J_{HH}$ = 8.4 Hz, 1H, 13-H), 7.55 (d, $^3J_{HH}$ = 8.2 Hz, 1H, 16-H), 7.48 (m, 1H, 15-H), 7.36 (m, 1H, 14-H), 6.92 (m, 1H, 3-H′), 6.91 (m, 1H, 4-H′), 6.69 (m, 1H, 4-H), 5.80 (m, 1H, 2-H′), 5.79 (m, 1H, 5-H′), 5.68 (m, 1H, 5-H), 5.60 (m, 1H, 2-H), 3.95 (s, 3H, 9-H), 2.69/2.66 (each m, each 1H, 6-H, 6-H′), 1.54 (m, 2H, 8-H), 1.37/1.31 (each m, each 1H, 7-H, 7-H′), 0.53/0.47 (each s, each 3H, Si(CH$_3$)$_2$), 0.01 (s, 9H, ^{a}Si-(CH$_3$)$_3$), −0.02 (s, 9H, ^{b}Si(CH$_3$)$_3$), 0.05/−0.10 (AB, $^2J_{HH}$ = 5.8 Hz, each 1H, ^{b}Si(CH$_2$)), −0.04/−0.29 (AB, $^2J_{HH}$ = 5.8 Hz, each 1H, ^{a}Si-(CH$_2$)). ^{13}C{^{1}H} NMR (d_2-dichloromethane, 150 MHz, 300 K): δ 138.2 ($^1J_{CF}$ = 238.8 Hz, *o*-C of C$_6$F$_5$), 131.4 (C10), 129.1 ($^1J_{CF}$ = 251.5 Hz, *p*-C of C$_6$F$_5$), 127.1 ($^1J_{CF}$ = 249.7 Hz, *m*-C of C$_6$F$_5$), 126.3 (C12), 125.3 (C3), 123.5 (C17), 115.5 (C14, C15), 111.4 (C4), 110.0 (C3′), 106.6 (C13), 107.1 (C4′), 102.9 (C2), 102.6 (C2′), 101.5 (C16), 100.8 (C5′), 100.7 (C5), 91.9 (C1′), 91.4 (C1), 38.4 (^{a}Si(CH$_2$)), 35.0 (^{b}Si(CH$_2$)), 23.7 (C9), 22.4 (C6), 18.5 (C7), 11.3 (C8), −4.6/−5.8 (Si(CH$_3$)$_2$), −6.9 (^{a}Si(CH$_3$)$_3$), −7.1 (^{b}Si(CH$_3$)$_3$), *ipso*-C of C$_6$F$_5$ not observed. ^{11}B{^{1}H} NMR (d_2-dichloromethane, 64 MHz, 298 K): δ = −5.16 ($ν_{1/2}$ = 346 Hz). ^{19}F NMR (d_2-dichloromethane, 564 MHz, 300 K): δ = −133.3 (m, 4F, *o*-F of C$_6$F$_5$), −160.4 (t, $^3J_{FF}$ = 20.2 Hz, 2F, *p*-F of C$_6$F$_5$), −165.1 (m, 4F, *m*-F of C$_6$F$_5$).

Reaction of Complex 4a with LDA; Formation of the Products 7 and 7′. d_8-Tetrahydrofuran was added at −78 °C to a mixture of **4a**

(73.4 mg, 85 μmol) and LDA (9.1 mg, 85 μmol). The mixture was slowly warmed to room temperature. The formation of the diastereo-isomeric products **7** and **7′** (1:1) was monitored by NMR, and these products were characterized spectroscopically from the mixture without isolating them. Diastereoisomer **7**, ^{1}H NMR (d_8-tetrahydrofuran, 600 MHz, 300 K): δ 7.83 (m, 1H, 16-H), 7.48 (m, 2H, 13-H, 15-H), 7.40 (m, 1H, 14-H), 6.80 (m, 1H, 3-H′), 6.79 (m, 1H, 4-H′), 6.28 (m, 1H, 4-H), 6.04 (m, 1H, 5-H′), 5.89 (m, 1H, 5-H), 5.81 (m, 1H, 2-H′), 5.43 (m, 1H, 2-H), 2.42 (m, 2H, 6-H), 1.56/1.37 (each m, each 1H, 8-H, 8-H′), 0.98/0.72 (each m, each 1H, 7-H, 7-H′), 0.69/0.60 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_8-tetrahydrofuran, 150 MHz, 300 K): δ 152.5 (C10), 143.3 (C3), 138.1 (C17), 133.6 (C12), 128.7 (C4′), 128.6 (C4), 126.8 (C3′), 126.1 (C14), 125.7 (C15), 115.2 (C2), 115.1 (C13), 115.0 (C5), 114.9 (C2′), 113.9 (C5′), 113.3 (C16), 108.7 (C1′), 108.1 (C1), 33.8 (C6), 33.0 (C9), 27.3 (C7), 21.3 (C8), −5.5/−5.7 (Si(CH$_3$)$_2$). Diastereoisomer **7′**, ^{1}H NMR (d_8-tetrahydrofuran, 600 MHz, 300 K): δ 7.83 (m, 1H, 16-H), 7.48 (m, 2H, 13-H, 15-H), 7.40 (m, 1H, 14-H), 6.85 (m, 1H, 3-H′), 6.79 (m, 1H, 4-H′), 6.21 (m, 1H, 4-H), 6.04 (m, 1H, 5-H′), 5.86 (m, 1H, 5-H), 5.84 (m, 1H, 2-H′), 5.47 (m, 1H, 2-H), 4.34/4.32 (each d, each $^nJ_{HF}$ = 3.4 Hz, each 3H, 9-H), 2.47/2.38 (each m, each 1H, 6-H, 6-H′), 1.45 (m, 2H, 8-H), 0.93/0.83 (each m, each 1H, 7-H, 7-H′), 0.69/0.62 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_8-tetrahydrofuran, 150 MHz, 300 K): δ 152.5 (C10), 143.3 (C3), 138.1 (C17), 133.6 (C12), 128.7 (C4′), 128.5 (C4), 127.0 (C3′), 126.1 (C14), 125.7 (C15), 115.2 (C5), 115.1 (C2), 115.1 (C13), 114.8 (C2′), 113.9 (C5′), 113.3 (C16), 108.7 (C1′), 108.0 (C1), 33.8 (C6), 33.0 (C9), 27.1 (C7), 21.1 (C8), −5.5/−5.7 (Si(CH$_3$)$_2$). The ^{1}H NMR of 9-H, ^{13}C NMR of B(C$_6$F$_5$)$_2$, ^{11}B NMR, and ^{19}F NMR resonances could not be assigned specifically to the single isomers. ^{1}H NMR (d_8-tetrahydrofuran, 600 MHz, 300 K): δ 4.34/4.32 (each d, each $^nJ_{HF}$ = 3.4 Hz, each 3H, 9-H). ^{13}C{^{1}H} NMR (d_8-tetrahydrofuran, 150 MHz, 300 K): δ 149.9 ($^1J_{CF}$ = 243.7 Hz, o-C of C$_6$F$_5$), 140.2 ($^1J_{CF}$ = 246.8 Hz, p-C of C$_6$F$_5$), 137.8 ($^1J_{CF}$ = 243.7 Hz, m-C of C$_6$F$_5$) ($ipso$-C of C$_6$F$_5$ was not observed; no assignment of the anellated C$_6$F$_4$-ring). ^{11}B{^{1}H} NMR (d_8-tetrahy-drofuran, 64 MHz, 298 K): δ = −4.40 ($\nu_{1/2}$ = 274 Hz). ^{19}F NMR (d_8-tetrahydrofuran, 564 MHz, 300 K): δ −132.6, −135.8, −151.7, −159.3 (each m, each 1F, 2-, 5-, 4-, 3-F of C$_6$F$_4$), −133.5 (m, 2F, o-F of C$_6$F$_5$), −134.2 (m, 2F, o-F′ of C$_6$F$_5$), −160.2 (t, $^3J_{FF}$ = 20.1 Hz, 1F, p-F of C$_6$F$_5$), −161.1 (t, $^3J_{FF}$ = 20.0 Hz, 1F, p-F′ of C$_6$F$_5$), −165.5 (m, 2F, m-F of C$_6$F$_5$), −165.9 (m, 2F, m-F′ of C$_6$F$_5$).

Reaction of Complex 1 with Phenyllithium; Synthesis of 8. Diethyl ether was added at −40 °C to a mixture of the zirconocene dichloride complex **1** (1.01 g, 2.60 mmol) and phenyllithium (0.44 g, 5.20 mmol). The mixture was warmed to 0 °C and stirred for 2 h. The solvent was removed in vacuo, and the residue was taken up in toluene and filtered through Celite. The solvent was removed from the clear filtrate in vacuo to yield 1.18 g (96%) of complex **8** as a slightly yellow solid, mp 114 °C. Anal. Calcd for C$_{27}$H$_{28}$SiZr (471.8): C, 68.73; H, 5.98. Found: C, 67.69; H, 5.81%. ^{1}H NMR (d_8-toluene, 600 MHz, 300 K): δ 7.44, 7.15, 7.06 (each m, 5H, o-, m-, p-H of [b]Ph), 7.20, 7.12, 6.99 (each m, 5H, o-, m-, p-H of [a]Ph), 6.48 (m, 1H, 3-H′), 6.37 (m, 1H, 4-H′), 6.34 (m, 1H, 4-H), 5.51 (m, 1H, 5-H′), 5.56 (m, 1H, 5-H), 5.54 (m, 1H, 2-H′), 5.50 (m, 1H, 7-H), 5.32 (m, 1H, 2-H), 4.72 (dm, $^3J_{HH}$ = 10.1 Hz, 1H, 8-H), 4.64 (dm, $^3J_{HH}$ = 17.0 Hz, 1H, 8-H′), 2.56/2.44 (each ABX, $^2J_{HH}$ = 16.2 Hz, each 1H, 6-H, 6-H′), 0.22 (s, 6H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_8-toluene, 150 MHz, 300 K): δ 186.0, 134.6, 127.2, 125.8 ($ipso$-, o-, m-, p-C of [a]Ph), 181.7, 136.9, 126.5, 126.0 ($ipso$-, o-, m-, p-C of [b]Ph), 137.5 (C7), 135.7 (C3), 123.6 (C4′), 123.1 (C4), 121.4 (C3′), 115.2 (C8), 114.8 (C2), 114.1 (C2′), 113.7 (C5), 112.7 (C5′), 100.6 (C1), 100.2 (C1′), 34.1 (C6), −5.8 (Si(CH$_3$)$_2$).

Thermolysis of Complex 8; Formation of the Products 10 and 11. NMR Experiment. A solution of 15.0 mg (3.18 μmol) of the diphenylzirconocene complex **8** in d_{12}-cyclohexane (or alternatively in d_6-benzene with ca. 10 mol equiv of PMe$_3$ added) was kept for 3 h at 80 °C. The obtained product (**10**) was characterized spectroscopically. ^{1}H NMR (d_{12}-cyclohexane, 600 MHz, 300 K): δ 7.12 (m, 1H, 3-H′),

6.89 (m, 1H, 4-H′), 6.83 (m, 1H, 12-H), 6.82 (m, 1H, 11-H), 6.74 (m, 1H, 14-H), 6.72 (m, 1H, 13-H), 6.20 (m, 1H, 4-H), 5.69 (m, 1H, 5-H′), 5.64 (m, 1H, 2-H′), 5.60 (m, 1H, 5-H), 5.19 (m, 1H, 2-H), 3.68 (m, 1H, 7-H), 2.97/2.83 (each m, each 1H, 6-H, 6-H′), 1.19/0.60 (each m, each 1H, 8-H, 8-H′), 0.56/ 0.40 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H}-NMR (d_{12}-cyclohexane, 150 MHz, 300 K): δ 181.2 (C10), 156.0 (C9), 134.9 (C11), 130.4 (C3), 127.2 (C12), 126.8 (C14), 124.6 (C13), 124.5 (C4), 120.2 (C3′), 117.6 (C4′), 116.5 (C2), 113.7 (C2′), 112.2 (C5′), 110.2 (C5), 102.1 (C1′), 98.0 (C1), 57.8 (C8), 45.5 (C7), 38.6 (C6), −4.4/−6.4 (Si(CH$_3$)$_2$).

Formation of 11 on a Preparative Scale. A solution containing 67.8 mg (144 μmol) of the diphenylzirconocene complex **8** and 10 mol equiv of PMe$_3$ in benzene was kept for 3 h at 80 °C. A suspension of 46.1 mg (294 μmol) of N,N-dimethylanilinium chloride in benzene was added at room temperature. The mixture was stirred for 24 h and then filtered through Celite. Removal of the solvent from the clear filtrate gave 59.8 mg (89%) of **11**, mp 132 °C. Anal. Calcd for C$_{21}$H$_{24}$-Cl$_2$SiZr (466.6): C, 54.05; H, 5.18. Found: C, 53.74; H, 5.05. ^{1}H NMR (d_6-benzene, 600 MHz, 300 K): δ 7.08 (m, 2H, 11-H), 7.02 (m, 2H, 12-H), 6.92 (m, 2H, 10-H), 6.85 (m, 1H, 3-H′), 6.75 (m, 1H, 4-H′), 6.26 (m, 1H, 4-H), 5.49 (m, 1H, 5-H′), 5.40 (m, 1H, 2-H′), 5.39 (m, 1H, 5-H), 5.18 (m, 1H, 2-H), 3.06/3.00 (each m, each 1H, 6-H, 6-H′), 2.76 (m, 1H, 7-H), 1.17 (d, $^3J_{HH}$ = 7.0 Hz, 3H, 8-H), 0.10/0.06 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 150 MHz, 300 K): δ 146.2 (C9), 140.7 (C3), 128.9 (C4), 128.5 (C11), 127.7 (C4′), 127.4 (C3′), 127.3 (C10), 126.2 (C12), 115.7 (C2′), 114.8 (C5), 114.2 (C2), 113.7 (C5′), 107.7 (C1), 107.1 (C1′), 41.8 (C7), 39.4 (C6), 22.1 (C8), −5.8/−6.1 (Si(CH$_3$)$_2$).

Addition of HB(C$_6$F$_5$)$_2$ to Complex 8; Generation of 12. The diphenylzirconocene complex **8** (27.8 mg, 59 μmol) and HB(C$_6$F$_5$)$_2$ (20.4 mg, 59 μmol) were dissolved in d_8-toluene. The hydroboration reaction is instantaneous. The product **12** was immediately characterized spectroscopically using this solution. ^{1}H NMR (d_8-toluene, 600 MHz, 300 K): δ 7.41, 7.15, 7.06 (each m, 5H, o-, m-, p-H of [b]Ph), 7.20, 7.14, 7.02 (each m, 5H, o-, m-, p-H of [a]Ph), 6.46 (m, 1H, 3-H′), 6.34 (m, 1H, 4-H′), 6.31 (m, 1H, 4-H), 5.55 (m, 1H, 5-H), 5.54 (m, 1H, 2-H′), 5.48 (m, 1H, 5-H′), 5.29 (m, 1H, 2-H), 1.88/1.70 (each m, each 1H, 6-H, 6-H′), 1.62 (m, 2H, 8-H), 1.40 (m, 2H, 7-H), 0.23 (s, 6H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_8-toluene, 150 MHz, 300 K): δ 186.0, 134.6, 127.3, 125.8 ($ipso$-, o-, m-, p-C of [a]Ph), 181.6, 136.0, 126.6, 126.2 ($ipso$-, o-, m-, p-C of [b]Ph), 147.0 ($^1J_{CF}$ = 250.1 Hz, o-C of C$_6$F$_5$), 143.4 ($^1J_{CF}$ = 253.2 Hz, p-C of C$_6$F$_5$), 137.6 ($^1J_{CF}$ = 250.1 Hz, m-C of C$_6$F$_5$), 136.9 (C3), 123.9 (C4′), 122.6 (C4), 121.5 (C3′), 114.3 (C2′), 114.2 (C2), 113.8 (C5), 112.7 (C5′), 101.1 (C1), 100.3 (C1′), 32.3 (C6), 31.8 (C8), 26.9 (C7), −5.8 (Si(CH$_3$)$_2$), ($ipso$-C of C$_6$F$_5$ was not observed). ^{11}B{^{1}H} NMR (d_8-toluene, 64 MHz, 298 K): δ 79.2. ^{19}F NMR (d_8-toluene, 564 MHz, 300 K): δ −129.7 (m, 4F, o-F of C$_6$F$_5$), −147.5 (t, $^3J_{FF}$ = 21.7 Hz, 2F, p-F of C$_6$F$_5$), −160.9 (m, 4F, m-F of C$_6$F$_5$).

Reaction of Complex 8 with HB(C$_6$F$_5$)$_2$; Formation of 14 and Preparation of 15. A solution containing 125 mg (265 μmol) of the diphenylzirconocene complex **8** and 91.8 mg (265 μmol) of HB(C$_6$F$_5$)$_2$ in toluene was stirred for 3 d at room temperature. The solvent was removed in vacuo to give **14** (174 mg, 89%) as a yellow solid, which was characterized spectroscopically. ^{1}H NMR (d_8-toluene, 600 MHz, 300 K): δ 7.21, 7.20, 7.04 (each m, 5H, o-, m-, p-H of Ph), 6.44 (m, 2H, 4-H′, 5-H), 6.35 (m, 1H, 5-H′), 5.95 (m, 1H, 3-H′), 5.80 (m, 1H, 2-H), 5.79 (m, 1H, 2-H′), 2.32/1.68 (each m, each 1H, 6-H, 6-H′), 1.56/ 1.23 (each m, each 1H, 8-H, 8-H′), 1.46/1.30 (each m, each 1H, 7-H, 7-H′), 0.65/0.61 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_8-toluene, 150 MHz, 300 K): δ 189.3, 128.6, 128.3, 127.6 ($ipso$-, o-, m-, p-C of Ph), 151.9 (C3), 125.0 (C5′), 121.6 (C4′), 119.8 (C5), 118.8 (C2), 115.2 (C2′), 112.4 (C3′), 105.0 (C1), 99.9 (C1′), 27.8 (C6), 24.3 (C8), 22.8 (C7), −5.5/−5.6 (Si(CH$_3$)$_2$) (C4 and C of C$_6$F$_5$ were not observed). ^{19}F NMR (d_8-toluene, 564 MHz, 300 K): δ −130.3 (br, 4F, o-F of C$_6$F$_5$), −156.1 (br, 2F, p-F of C$_6$F$_5$), −162.6 (br, 4F, m-F of C$_6$F$_5$).

The temperature-dependent ^{19}F NMR spectra revealed a conformational equilibration between **14A** and **14B**. Conformer **14A**, ^{19}F NMR (d_8-toluene, 564 MHz, 203 K): δ −126.2, −175.4 (each br, each 1F, *o*-F of C$_6$F$_5$), −131.2, −132.1 (br, 2F, *o*-F′ of C$_6$F$_5$), −155.6, −164.2 (each m, each 1F, *m*-F of C$_6$F$_5$), −156.8 (br, 1F, *p*-F of C$_6$F$_5$), −160.0 (br, 1F, *p*-F′ of C$_6$F$_5$), −162.8, −164.6 (each m, each 1F, *m*-F′ of C$_6$F$_5$). ^{19}F/^{19}F GCOSY (d_8-toluene, 564/564 MHz, 203 K): δ (^{19}F)/δ (^{19}F) −126.2/−164.2 (*o*-F/*m*-F), −131.2/−164.6 (*o*-F′/*m*-F′), −132.1/−162.8 (*o*-F′/*m*-F′), −155.6/−175.4, −156.8 (*m*-F/*o*-F, *p*-F), −156.8/−155.6, −164.2 (*p*-F/*m*-F), −160.0/−162.8, −164.6 (*p*-F′/*m*-F′), −162.8/−132.1, −160.0 (*m*-F′/*o*-F′, *p*-F′), −164.2/−126.2, −156.8 (*m*-F/*o*-F, *p*-F), −164.6/−131.2, −160.0 (*m*-F′/*o*-F′, *p*-F′), −175.4/−155.6 (*o*-F/*m*-F). Conformer **B**, ^{19}F NMR (d_8-toluene, 564 MHz, 203 K): δ −108.6, −111.2 (each br, each 1F, *o*-F of C$_6$F$_5$), −129.6, (br, 2F, *o*-F′ of C$_6$F$_5$), −150.0 (br, 1F, *p*-F′ of C$_6$F$_5$), −154.7 (br, 1F, *p*-F of C$_6$F$_5$), −160.0, −161.5 (each m, each 1F, *m*-F of C$_6$F$_5$), −161.1 (each br, each 1F, *m*-F′ of C$_6$F$_5$). ^{19}F/^{19}F GCOSY (d_8-toluene 564/564 MHz, 203 K): δ (^{19}F)/δ (^{19}F) −108.6/−160.0 (*o*-F/*m*-F), −111.2/−161.5 (*o*-F/*m*-F), −129.6/−161.1 (*o*-F′/*m*-F′), −150.0/−161.1 (*p*-F′/*m*-F′), −154.7/−160.0, −161.5 (*p*-F/*m*-F), −160.0/−108.6, −154.7 (*m*-F/*o*-F, *p*-F), −161.1/−129.6, −150.0 (*m*-F′/*o*-F′, *p*-F′), −161.5/−111.2, −154.7 (*m*-F/*o*-F, *p*-F). X-ray crystal structure analysis of complex **14A**: single crystals were obtained from a concentrated toluene solution at −20 °C, formula C$_{33}$H$_{23}$BF$_{10}$SiZr·C$_7$H$_8$, *M* = 831.77, yellow crystal 0.50 × 0.50 × 0.20 mm, *a* = 9.766(1), *b* = 10.662(1), *c* = 18.675(1) Å, α = 104.46(1), β = 96.15(1), γ = 109.47(1)°, *V* = 1736.2(3) Å^3, ρ_{calc} = 1.591 g cm^{-3}, μ = 4.36 cm^{-1}, empirical absorption correction (0.812 ≤ *T* ≤ 0.918), *Z* = 2, triclinic, space group *P*1 (No. 2), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 16 169 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.67 Å^{-1}, 8376 independent (R_{int} = 0.037) and 7283 observed reflections [*I* ≥ 2σ(*I*)], 480 refined parameters, *R* = 0.035, w*R*^{2} = 0.086, max. residual electron density 0.74 (−0.59) e Å^{-3}, hydrogens calculated and refined as riding atoms.

For the preparation of **15**, a solution containing 162 mg (343 μmol) of complex **8** and 119 mg (344 μmol) of HB(C$_6$F$_5$)$_2$ in toluene was stirred for 3 d at room temperature. A slight excess of PMe$_3$ was added, and then all volatiles were removed in vacuo to yield 250 mg (89%) of the product **15** as a yellow solid, mp 168 °C. Anal. Calcd for C$_{36}$H$_{32}$-BF$_{10}$PSiZr (815.7): C, 53.01; H, 3.95. Found: C, 52.53; H, 3.69. ^{1}H NMR (d_8-toluene, 600 MHz, 300 K): δ = 7.15, 7.12, 7.00 (each m, 5H, *m*-, *o*-, *p*-H of Ph), 6.71 (m, 1H, 4-H′), 6.09 (m, 1H, 5-H), 5.97 (m, 1H, 3-H′), 5.79 (m, 1H, 2-H), 5.74 (m, 1H, 5-H′), 5.53 (m, 1H, 2-H′), 2.30/1.96 (each m, each 1H, 6-H, 6-H′), 1.66/0.96 (each m, each 1H, 7-H, 7-H′), 1.31/0.85 (each m, each 1H, 8-H, 8-H′), 0.35/0.31 (each s, each 3H, Si(CH$_3$)$_2$), 0.22 (d, $^2J_{PH}$ = 10.1 Hz, 9H, PMe$_3$). ^{13}C{^{1}H} NMR (d_8-toluene, 150 MHz, 300 K): δ = 186.7, 131.4, 127.0, 126.0 (*ipso*-, *o*-, *m*-, *p*-C of Ph), 149.0 ($^1J_{CF}$ = 238.3 Hz, *o*-C of C$_6$F$_5$), 144.3 (C3), 139.5 ($^1J_{CF}$ = 261.6 Hz, *p*-C of C$_6$F$_5$), 137.7 ($^1J_{CF}$ = 263.0 Hz, *m*-C of C$_6$F$_5$), 125.0 (C3′), 120.2 (C4′), 119.4 (C2), 116.3 (C5), 115.4 (C2′), 109.6 (C5′), 99.7 (C1), 97.4 (C1′), 28.5 (C6), 24.3 (C7), 16.2 (C8), 8.9 (d, $^1J_{CP}$ = 30.2 Hz, PMe$_3$), −4.9/−5.8 (Si(CH$_3$)$_2$) (C4 and *ipso*-C of C$_6$F$_5$ were not observed). ^{11}B{^{1}H} NMR (d_8-toluene, 64 MHz, 300 K): δ = −13.0 ($\nu_{1/2}$ = 224 Hz). ^{31}P{^{1}H} NMR (d_8-toluene, 81 MHz, 300 K): δ = −9.4 ($\nu_{1/2}$ = 0.3 Hz). ^{19}F NMR (d_8-toluene, 564 MHz, 300 K): δ = −106.3, −109.5 (each br, each 1F, *o*-F of C$_6$F$_5$), −124.9 (br, 2F, *o*-F of C$_6$F$_5$), −156.9, −157.8 (each t, $^3J_{FF}$ = 20.1 Hz, each 1F, *p*-F of C$_6$F$_5$), −161.9, −162.2 (each m, each 1F, *m*-F of C$_6$F$_5$), −163.1 (m, 2F, *m*-F of C$_6$F$_5$).

Reaction of Complex 12 with *n*-Butylisocyanide; Preparation of the Insertion Product 16. At room temperature, a solution of 73 mg (0.88 mmol) of *n*-butylisocyanide was added dropwise with stirring to a solution of freshly generated complex **12** (347 mg, 0.42 mmol) in toluene. The mixture was stirred for 2 h, and then all volatiles were removed in vacuo to give complex **16** (385 mg, 92%) as a pale yellow solid, mp 147 °C (decomp.). Anal. Calcd for C$_{49}$H$_{47}$N$_2$BF$_{10}$SiZr (984.9): C, 59.81; H, 4.81; N, 2.85. Found: C, 58.87; H, 4.63; N,

2.68. ^{1}H NMR (d_6-benzene, 600 MHz, 300 K): δ 7.97, 7.44, 7.28 (each m, 5H, *o*-, *m*-, *p*-H of ^{a}Ph), 6.96, 7.23, 7.07 (each m, 5H, *o*-, *m*-, *p*-H of ^{b}Ph), 6.52 (m, 1H, 3-H′), 6.03 (m, 1H, 5-H), 5.99 (m, 1H, 5-H′), 5.75 (m, 1H, 2-H′), 5.43 (m, 1H, 2-H), 5.25 (m, 1H, 4-H′), 5.19 (m, 1H, 4-H), 3.58 (m, 2H, 13-H), 2.21 (m, 2H, 9-H), 2.04 (m, 2H, 6-H), 1.51/1.30 (each m, each 1H, 14-H, 14-H′), 1.44/1.35 (m, 2H, 7-H, 7-H′), 1.44/1.33 (m, 2H, 8-H, 8-H′), 1.03 (m, 2H, 15-H), 0.78 (m, 2H, 10-H), 0.75 (m, 2H, 11-H), 0.68 (t, $^3J_{HH}$ = 7.3 Hz, 3H, 16-H), 0.43 (t, $^3J_{HH}$ = 7.2 Hz, 3H, 12-H), 0.40/0.26 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 150 MHz, 300 K): δ 240.1 (Zr−C≡N), 179.1, 141.8, 126.7, 123.9 (*ipso*-, *o*-, *m*-, *p*-C of ^{a}Ph), 148.2 ($^1J_{CF}$ = 245.7 Hz, *o*-C of C$_6$F$_5$), 142.6, 129.8, 127.4, 123.1 (*ipso*-, *m*-, *p*-, *o*-C of ^{b}Ph), 139.9 ($^1J_{CF}$ = 250.1 Hz, *p*-C of C$_6$F$_5$), 138.8 (C3), 137.6 ($^1J_{CF}$ = 261.0 Hz, *m*-C of C$_6$F$_5$), 117.7 (*ipso*-C of C$_6$F$_5$), 121.9 (C3′), 112.1 (C4′), 111.9 (C4), 108.1 (C5), 107.6 (C5′), 105.6 (C2′), 105.4 (C2), 102.3 (C1), 102.0 (C1′), 48.6 (C13), 43.0 (C9), 33.6 (C6), 31.2 (C14), 30.9 (C7), 29.2 (C10), 20.7 (C8), 20.5 (C15), 19.1 (C11), 13.5 (C16), 12.6 (C12), −4.4/−6.3 (Si(CH$_3$)$_2$) (B−CN not observed). ^{11}B{^{1}H} NMR (d_6-benzene, 64 MHz, 298 K): δ = −18.5 ($\nu_{1/2}$ = 232 Hz). ^{19}F NMR (d_6-benzene, 564 MHz, 300 K): δ = −132.8 (m, 4F, *o*-F of C$_6$F$_5$), −157.4 (t, $^3J_{FF}$ = 20.7 Hz, 2F, *p*-F of C$_6$F$_5$), −163.2 (m, 4F, *m*-F of C$_6$F$_5$).

Addition of PMe$_3$ to Complex 12; Preparation of 17. Trimethylphosphine (24 mg, 315 μmol) was added to a freshly prepared solution of the diphenylzirconocene/borane complex **12** (49 mg, 60 μmol) in toluene at room temperature. The mixture was stirred for 1 h, and then all volatiles were removed in vacuo to yield 52 mg (97%) of **17** as a light yellow solid, mp 227 °C (decomp.). Anal. Calcd for C$_{42}$H$_{38}$BF$_{10}$-PSiZr (893.8): C, 56.44; H, 4.29. Found: C, 56.10; H, 4.41%. ^{1}H NMR (d_6-benzene, 600 MHz, 300 K): δ = 7.52, 7.23, 7.13 (each m, 5H, *o*-, *m*-, *p*-H of ^{b}Ph), 7.31, 7.20, 7.08 (each m, 5H, *o*-, *m*-, *p*-H of ^{a}Ph), 6.52 (m, 1H, 3-H′), 6.45 (m, 1H, 4-H′), 6.45 (m, 1H, 4-H), 5.63 (m, 1H, 5-H), 5.62 (m, 1H, 2-H′), 5.58 (m, 1H, 5-H′), 5.41 (m, 1H, 2-H), 2.01/1.89 (each m, each 1H, 6-H, 6-H′), 1.22/1.09 (each m, each 1H, 7-H, 7-H′), 0.74 (m, 2H, 8-H), 0.38 (d, $^2J_{PH}$ = 10.7 Hz, 9H, PMe$_3$), 0.27/0.26 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 150 MHz, 300 K): δ 186.2, 134.4, 126.8, 125.5 (*ipso*-, *o*-, *m*-, *p*-C of ^{a}Ph), 181.7, 136.2, 126.4, 125.9 (*ipso*-, *o*-, *m*-, *p*-C of ^{b}Ph), 148.1 ($^1J_{CF}$ = 236.4 Hz, *o*-C of C$_6$F$_5$), 139.4 ($^1J_{CF}$ = 251.3 Hz, *p*-C of C$_6$F$_5$), 138.4 (C3), 137.4 ($^1J_{CF}$ = 253.6 Hz, *m*-C of C$_6$F$_5$), 123.2 (C4′), 123.2 (C4), 121.5 (C3′), 119.7 (*ipso*-C of C$_6$F$_5$), 114.7 (C2), 114.3 (C2′), 113.2 (C5), 112.1 (C5′), 100.4 (C1), 100.3 (C1′), 33.2 (C6), 29.4 (C7), 20.0 (C8), 8.9 (d, $^1J_{CP}$ = 37.2 Hz, PMe$_3$), −5.5/−5.8 (Si(CH$_3$)$_2$). ^{11}B{^{1}H} NMR (d_6-benzene, 64 MHz, 298 K): δ −14.1 ($\nu_{1/2}$ = 258 Hz). ^{31}P-{^{1}H} NMR (d_6-benzene, 81 MHz, 300 K): δ −10.2 ($\nu_{1/2}$ = 115 Hz). ^{19}F NMR (d_6-benzene, 564 MHz, 300 K): δ = −130.7 (m, 2F, *o*-F of C$_6$F$_5$), −130.8 (m, 2F, *o*-F′ of C$_6$F$_5$), −158.3 (t, $^3J_{FF}$ = 20.8 Hz, 2F, *p*-F of C$_6$F$_5$), −163.6 (m, 4F, *m*-F of C$_6$F$_5$).

Thermolysis of Complex 12 in the Presence of Excess PMe$_3$; Preparation of the (Aryne)zirconocene Complex 18. A 10-fold excess of PMe$_3$ was added to a solution of 49 mg (60 μmol) of freshly generated **12** in toluene at room temperature. The reaction mixture was then kept for 3 h at 80 °C. Volatiles were removed in vacuo at ambient temperature to yield 49 mg (92%) of complex **18** as a pale yellow solid, mp 224 °C (decomp.). Anal. Calcd for C$_{39}$H$_{41}$BF$_{10}$P$_2$SiZr (891.8): C, 52.53; H, 4.63. Found: C, 52.53; H, 3.69. ^{1}H NMR (d_6-benzene, 600 MHz, 300 K): δ 8.09 (m, 1H, 11-H), 7.66 (m, 1H, 14-H), 7.33 (m, 2H, 12-H, 13-H), 6.28 (m, 1H, 2-H′), 6.02 (m, 1H, 2-H), 5.26 (m, 2H, 4-H, 5-H′), 5.25 (m, 1H, 4-H′), 5.19 (m, 1H, 5-H), 5.16 (m, 1H, 3-H′), 1.53/1.29 (each m, each 1H, 6-H, 6-H′), 1.08 (d, $^2J_{PH}$ = 6.1 Hz, 9H, Zr−PMe$_3$), 1.07/0.74 (each m, each 1H, 7-H, 7-H′), 0.54 (m, 2H, 8-H), 0.38 (d, $^2J_{PH}$ = 11.4 Hz, 9H, B−PMe$_3$), 0.48/0.37 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 150 MHz, 300 K): δ 178.5 (C10), 157.8 (C9), 148.1 ($^1J_{CF}$ = 241.3 Hz, *o*-C of C$_6$F$_5$), 139.4 ($^1J_{CF}$ = 252.4 Hz, *p*-C of C$_6$F$_5$), 137.5 ($^1J_{CF}$ = 257.8 Hz, *m*-C of C$_6$F$_5$), 134.1 (C14), 132.3 (C3), 131.6 (C11), 127.4 (C12, C13), 119.9 (*ipso*-C

of C_6F_5), 114.2 (C3′), 109.6 (C4), 108.5 (C4′), 106.9 (C2), 106.2 (C2′), 101.5 (C1′), 100.5 (C5′), 100.2 (C1), 99.8 (C5), 33.0 (C6), 28.0 (C7), 20.4 (C8), 18.2 (d, $^1J_{CP}$ = 17.4 Hz, Zr–PMe$_3$), 8.8 (d, $^1J_{CP}$ = 36.6 Hz, B–PMe$_3$), −4.8/−5.1 (Si(CH$_3$)$_2$). ^{11}B{^{1}H} NMR (d_6-benzene, 64 MHz, 298 K): δ −14.0 ($\nu_{1/2}$ = 258 Hz). ^{31}P{^{1}H} NMR (d_6-benzene, 81 MHz, 300 K): δ −7.9 (Zr–PMe$_3$, $\nu_{1/2}$ = 7 Hz), −10.0 (B–PMe$_3$, $\nu_{1/2}$ = 120 Hz). ^{19}F NMR (d_6-benzene, 564 MHz, 300 K): δ −129.9 (m, 2F, o-F of C_6F_5), −130.3 (m, 2F, o-F′ of C_6F_5), −157.9 (t, $^3J_{FF}$ = 20.7 Hz, 1F, p-F′ of C_6F_5), −158.4 (t, $^3J_{FF}$ = 20.8 Hz, 1F, p-F of C_6F_5), −163.1 (m, 2F, m-F′ of C_6F_5), −163.2 (m, 2F, m-F of C_6F_5). ^{19}F/^{19}F GCOSY (d_6-benzene, 564/564 MHz, 300 K): δ (^{19}F)/δ (^{19}F) −129.9/−163.2 (o-F/m-F), −130.3/−163.1 (o-F′/m-F′), −158.4/−163.2 (p-F/m-F), −157.9/−163.1 (p-F′/m-F′), −163.1/−157.9, −130.3 (m-F/p-F, o-F), −163.2/−158.4, −129.9 (m-F/p-F, o-F).

Reaction of Complex 12 with *N*-Methylbenzimidazole; Preparation of 19a. A solution of 41 mg (313 μmol) of 1-methylbenzimidazole in 10 mL of toluene was added to a solution of 256 mg (313 μmol) of freshly generated **12** in 50 mL of toluene at room temperature. The solvent was removed after 1 h to yield 294 mg (99%) of the product **19a** as a yellow solid, mp 181 °C (decomp.). Anal. Calcd for C$_{47}$H$_{37}$N$_2$BF$_{10}$SiZr (949.9): C, 59.43; H, 3.93; N, 2.95. Found: C, 59.34; H, 4.19; N, 3.11. ^{1}H NMR (d_6-benzene, 600 MHz, 300 K): δ 7.72 (m, 1H, 13-H), 7.56, 7.26, 7.15 (each m, 5H, o-, m-, p-H of ^{b}Ph), 7.36 (s, 1H, 10-H), 7.35, 7.26, 7.12 (each m, 5H, o-, m-, p-H of ^{a}Ph), 6.85 (m, 1H, 14-H), 6.83 (m, 1H, 15-H), 6.58 (m, 1H, 3-H′), 6.52 (m, 1H, 4-H), 6.47 (m, 1H, 4-H′), 6.43 (m, 1H, 16-H), 5.66 (m, 1H, 5-H), 5.64 (m, 1H, 2-H′), 5.60 (m, 1H, 5-H′), 5.48 (m, 1H, 2-H), 2.21 (s, 3H, 9-H), 2.12/1.94 (each m, each 1H, 6-H, 6-H′), 1.49 (m, 2H, 8-H), 1.23/1.19 (each m, each 1H, 7-H, 7-H′), 0.28/0.25 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 150 MHz, 300 K): δ 186.1, 134.4, 126.5, 125.7 (*ipso*-, o-, m-, p-C of ^{a}Ph), 181.7, 136.3, 126.5, 126.1 (*ipso*-, o-, m-, p-C of ^{b}Ph), 148.6 ($^1J_{CF}$ = 241.7 Hz, o-C of C_6F_5), 141.2 (C10), 139.6 ($^1J_{CF}$ = 256.8 Hz, p-C of C_6F_5), 138.9 (C3), 137.5 ($^1J_{CF}$ = 253.0 Hz, m-C of C_6F_5), 136.3 (C12), 132.7 (C17), 125.4 (C14), 125.1 (C15), 123.5 (C4′), 123.1 (C4), 121.8 (C3′), 116.7 (C13), 114.9 (C2), 114.3 (C2′), 113.5 (C5), 112.4 (C5′), 110.7 (C16), 100.5 (C1), 100.1 (C1′), 33.4 (C6), 30.6 (C9), 28.5 (C7), 21.7 (C8), −5.8/−6.2 (Si(CH$_3$)$_2$) (*ipso*-C of C_6F_5 not observed). ^{11}B{^{1}H} NMR (d_6-benzene, 64 MHz, 298 K): δ −4.54 ($\nu_{1/2}$ = 383 Hz). ^{19}F NMR (d_6-benzene, 564 MHz, 300 K): δ −132.7 (m, 4F, o-F of C_6F_5), −158.5 (t, $^3J_{FF}$ = 21.1 Hz, 1F, p-F of C_6F_5), −158.6 (t, $^3J_{FF}$ = 21.1 Hz, 1F, p-F′ of C_6F_5), −164.2 (m, 4F, m-F of C_6F_5).

Reaction of Complex 12 with 1,2-Dimethylbenzimidazole; Preparation of 19b. A solution containing 29 mg (195 μmol) of 1,2-dimethylbenzimidazole in 10 mL of toluene was added to a freshly prepared solution of 159 mg (195 μmol) of **12** in 30 mL of toluene. The solvent was removed in vacuo after 1 h, and the product was dried in vacuo, to yield 189 mg (99%) of **19b** as a yellow powder, mp 170 °C (decomp.). Anal. Calcd for C$_{48}$H$_{39}$N$_2$BF$_{10}$SiZr (964.0): C, 59.81; H, 4.08; N, 2.91. Found: C, 59.69; H, 4.27; N, 2.79. ^{1}H NMR (d_6-benzene, 600 MHz, 300 K): δ 7.67 (m, 1H, 13-H), 7.53, 7.22, 7.14 (each m, 5H, o-, m-, p-H of ^{b}Ph), 7.33, 7.21, 7.07 (each m, 5H, o-, m-, p-H of ^{a}Ph), 6.92 (m, 1H, 14-H), 6.90 (m, 1H, 15-H), 6.54 (m, 1H, 3-H′), 6.46 (m, 1H, 16-H), 6.45 (m, 1H, 4-H′), 6.43 (m, 1H, 4-H), 5.63 (m, 1H, 2-H′), 5.61 (m, 1H, 5-H), 5.55 (m, 1H, 5-H′), 5.43 (m, 1H, 2-H), 2.09/1.99 (each m, each 1H, 6-H, 6-H′), 2.08 (s, 3H, 9-H), 1.75 (s, 3H, Me-10), 1.59 (m, 2H, 8-H), 1.23/1.15 (each m, each 1H, 7-H, 7-H′), 0.25/0.23 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 150 MHz, 300 K): δ 186.2, 134.3, 126.8, 125.6 (*ipso*-, o-, m-, p-C of ^{a}Ph), 181.7, 136.4, 126.3, 125.8 (*ipso*-, o-, m-, p-C of ^{b}Ph), 151.8 (C10), 148.5 ($^1J_{CF}$ = 240.4 Hz, o-C of C_6F_5), 139.5 ($^1J_{CF}$ = 248.3 Hz, p-C of C_6F_5), 138.5 (C3), 137.5 ($^1J_{CF}$ = 251.1 Hz, m-C of C_6F_5), 136.2 (C12), 132.1 (C17), 124.5 (C14), 124.2 (C15), 123.6 (C4′), 123.2 (C4), 122.7 (*ipso*-C of C_6F_5), 121.1 (C3′), 117.7 (C13), 114.8 (C2), 114.3 (C2′), 113.2 (C5), 112.1 (C5′), 110.0 (C16), 100.3 (C1, C1′),

33.2 (C6), 28.9 (C7), 28.8 (C9), 22.9 (C8), 11.8 (Me10), −5.3/−5.6 (Si(CH$_3$)$_2$). ^{11}B{^{1}H} NMR (d_6-benzene, 64 MHz, 298 K): δ −3.30 ($\nu_{1/2}$ = 416 Hz). ^{19}F NMR (d_6-benzene, 564 MHz, 300 K): δ −132.1 (m, 4F, o-F of C_6F_5), −158.5 (t, $^3J_{FF}$ = 22.0 Hz, 1F, p-F of C_6F_5), −158.6 (t, $^3J_{FF}$ = 22.0 Hz, 1F, p-F′ of C_6F_5), −163.7 (m, 4F, m-F of C_6F_5).

Thermolysis of 19a in the Presence of *N*-Methylbenzimidazole; Formation of 20. A solution of 50 mg (53 μmol) of complex **19a** and 7 mg (53 μmol) of 1-methylbenzimidazole in benzene was kept for 3 h at 80 °C. The solvent was then removed in vacuo at room temperature, and the product was dried in vacuo, to yield complex **20** (48 mg, 90%), a yellow solid, as a mixture of two diastereoisomers (**20A**:**20B** = 3:2), mp 283 °C (decomp.). Anal. Calcd for C$_{49}$H$_{39}$N$_4$BF$_{10}$SiZr (1004.0): C, 58.62; H, 3.92; N, 5.58. Found: C, 58.54; H, 4.06; N, 5.10.

Diastereoisomer **20A**, ^{1}H NMR (d_6-benzene, 600 MHz, 300 K): δ 8.29, 7.52, 7.33 (each m, 5H, o-, m-, p-H of Ph), 8.01 (m, 1H, 13-H′), 7.69 (m, 1H, 13-H), 7.32 (s, 1H, 10-H), 7.14 (m, 1H, 15-H′), 7.12 (m, 1H, 14-H′), 6.97 (m, 1H, 16-H′), 6.83 (m, 2H, 14-H, 15-H), 6.57 (m, 1H, 3-H′), 6.46 (m, 1H, 16-H), 6.16 (m, 1H, 5-H), 6.08 (m, 1H, 5-H′), 5.84 (m, 1H, 2-H′), 5.55 (m, 1H, 2-H), 5.13 (m, 1H, 4-H′), 5.09 (m, 1H, 4-H), 3.37 (s, 3H, 9-H′), 2.31 (s, 3H, 9-H), 1.97/1.94 (each m, each 1H, 6-H, 6-H′), 1.45 (m, 2H, 8-H), 1.14 (m, 2H, 7-H), 0.46/0.44 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 150 MHz, 300 K): δ 181.4, 142.0, 127.0, 124.1 (*ipso*-, o-, m-, p-C of Ph), 202.9 (C10′), 148.5 ($^1J_{CF}$ = 238.4 Hz, o-C of C_6F_5), 143.6 (C17′), 141.2 (C10), 140.8 (C12′), 140.6 (C3), 139.4 ($^1J_{CF}$ = 251.5 Hz, p-C of C_6F_5), 137.5 ($^1J_{CF}$ = 249.6 Hz, m-C of C_6F_5), 136.4 (C12), 132.7 (C17), 127.3 (C14′), 125.4 (C14), 125.1 (C15), 122.9 (C3′), 122.7 (C15′), 121.7 (*ipso*-C of C_6F_5), 118.4 (C13′), 116.7 (C13), 114.4 (C4′), 114.0 (C4′), 110.9 (C16), 109.8 (C16′), 108.9 (C5), 108.8 (C2), 108.5 (C5′), 108.4 (C2′), 102.9 (C1), 102.8 (C1′), 33.3 (C6), 32.6 (C9′), 30.8 (C9), 28.7 (C7), 21.6 (C8), −4.2/−5.9 (Si(CH$_3$)$_2$). ^{11}B{^{1}H} NMR (d_6-benzene, 64 MHz, 298 K): δ −5.10 ($\nu_{1/2}$ = 341 Hz). ^{19}F NMR (d_6-benzene, 564 MHz, 300 K): δ −132.9 (m, 2F, o-F of C_6F_5), −133.2 (m, 2F, o-F′ of C_6F_5), −158.7 (t, $^3J_{FF}$ = 20.8 Hz, 1F, p-F of C_6F_5), −158.8 (t, $^3J_{FF}$ = 20.8 Hz, 1F, p-F′ of C_6F_5), −164.0 (m, 2F, m-F of C_6F_5), −164.1 (m, 2F, m-F′ of C_6F_5). ^{19}F–^{19}F GCOSY (d_6-benzene, 564/564 MHz, 300 K): δ (^{19}F)/δ (^{19}F) −132.9/−164.0 (o-F/m-F), −133.2/−164.1 (o-F′/m-F′), −158.7/−164.0 (p-F/m-F), −158.8/−164.1 (p-F′/m-F′), −164.0/−132.9, −158.7 (m-F/o-F, p-F), −164.1/−133.2, −158.8 (m-F′/o-F′, p-F′). Diastereoisomer **20B**, ^{1}H NMR (d_6-benzene, 600 MHz, 300 K): δ 8.30, 7.52, 7.33 (each m, 5H, o-, m-, p-H of Ph), 8.01 (m, 1H, 13-H′), 7.63 (m, 1H, 13-H), 7.19 (s, 1H, 10-H), 7.14 (m, 1H, 15-H′), 7.12 (m, 1H, 14-H′), 6.97 (m, 1H, 16-H′), 6.83 (m, 2H, 14-H, 15-H), 6.48 (m, 1H, 4-H′), 6.46 (m, 1H, 16-H), 6.35 (m, 1H, 4-H), 6.14 (m, 1H, 2-H′), 6.09 (m, 1H, 2-H), 5.83 (m, 1H, 5-H′), 5.74 (m, 1H, 5-H), 5.17 (m, 1H, 3-H′), 3.43 (s, 3H, 9-H′), 2.29 (s, 3H, 9-H), 1.55/1.15 (each m, each 1H, 6-H, 6-H′), 1.40/1.28 (each m, each 1H, 8-H, 8-H′), 0.90 (m, 2H, 7-H), 0.44/0.42 (each s, each 3H, Si(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (d_6-benzene, 150 MHz, 300 K): δ 177.2, 141.7, 126.8, 124.1 (*ipso*-, o-, m-, p-C of Ph), 202.7 (C10′), 148.5 ($^1J_{CF}$ = 238.4 Hz, o-C of C_6F_5), 143.6 (C17′), 141.2 (C10), 140.8 (C12′), 139.4 ($^1J_{CF}$ = 251.5 Hz, p-C of C_6F_5), 137.5 ($^1J_{CF}$ = 249.6 Hz, m-C of C_6F_5), 136.4 (C12), 132.7 (C17), 132.0 (C3), 127.3 (C14′), 125.4 (C14), 125.1 (C15), 124.5 (C4′), 124.4 (C4), 122.7 (C15′), 121.7 (*ipso*-C of C_6F_5), 118.4 (C13′), 116.5 (C13), 112.9 (C3′), 110.9 (C16), 110.8 (C2), 109.8 (C16′), 109.1 (C2′), 107.0 (C5′), 106.9 (C5), 103.5 (C1′), 102.6 (C1), 32.6 (C9′), 31.6 (C6), 30.8 (C9), 28.1 (C7), 20.9 (C8), −4.2/−6.1 (Si(CH$_3$)$_2$). ^{11}B{^{1}H} NMR (d_6-benzene, 64 MHz, 298 K): δ −5.1 ($\nu_{1/2}$ = 341 Hz). ^{19}F NMR (benzene-d_6, 564 MHz, 300 K): δ −132.9 (m, 2F, o-F of C_6F_5), −133.4 (m, 2F, o-F′ of C_6F_5), −158.6 (t, $^3J_{FF}$ = 20.8 Hz, 1F, p-F of C_6F_5), −158.9 (t, $^3J_{FF}$ = 20.8 Hz, 1F, p-F′ of C_6F_5), −163.9 (m, 2F, m-F of C_6F_5), −164.0 (m, 2F, m-F′ of C_6F_5). ^{19}F/^{19}F GCOSY (d_6-benzene, 564/564 MHz, 300 K): δ (^{19}F)/δ (^{19}F) −132.9/−163.9 (o-F/m-F), −133.4/

−164.0 (*o*-F′/*m*-F′), −158.6/−163.9 (*p*-F/*m*-F), −158.9/−164.0 (*p*-F′/ *m*-F′), −163.9/−132.9, −158.6 (*m*-F/*o*-F, *p*-F), −164.0/−133.4, −158.9 (*m*-F′/*o*-F′, *p*-F′).

Supporting Information Available: Additional spectroscopic data of the metallocene complexes **4**−**20** (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA048447L